

Differential Accumulation of Polychlorinated Biphenyl Congeners in the Terrestrial Food Web of the Kalamazoo River Superfund Site, Michigan

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A series of field studies was conducted to determine the bioaccumulation of polychlorinated biphenyl (PCB) congeners in the terrestrial food web of the Kalamazoo River flood plain. Samples included colocated soils, native plants likely to be consumed by wildlife, several taxa of terrestrial invertebrates, small mammals, passerine bird eggs, nestlings, and adults, and great horned owl plasma and eggs. Mean concentrations of total PCBs in samples from the former Trowbridge impoundment were 6.5 mg/kg dry weight for soils and 0.023, 0.13, 1.3, 1.3, 1.6, and 8.2 mg/kg wet weight for plants, small herbivorous mammals, depurated earthworms, shrews, great horned owl eggs, and house wren eggs, respectively. Historical data from the Kalamazoo River have reported Aroclor-equivalent total PCB concentrations in the terrestrial food web; however, the degree of environmental weathering of the parent PCB mixtures was unknown. In this study, earthworms and composite samples of coleoptera exhibited PCB congener patterns that were similar to patterns in colocated soils. However, in plants, less chlorinated PCBs (e.g., mono-, di-, tri-, and tetrachlorinated biphenyls) were predominant, and in small mammals, there was a notable enrichment of PCBs 153, 180, 138, 118, and 99. In general, concentrations of PCBs were lower in most biota than in soil from the

Kalamazoo River Area of Concern (KRAOC) although there was a modest biomagnification of PCBs from lower trophic level biota to higher trophic levels. As a consequence of environmental weathering of PCBs in the terrestrial food web of the KRAOC, the relative potency of the PCBs (expressed as mg TEQs/kg PCBs) decreased from soil to most biota. While there was a general trend, as expected, in which concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) increased with total PCBs, this relationship was rather poor ($R^2 = 0.13$). Taken together, these data suggest that the differential accumulation of PCB congeners in the terrestrial food web can be explained by congener-specific differences in bioavailability from soil, exposure pathways, and metabolic potential of each of the food web components.

Introduction

In 1990, approximately 80 miles of the Kalamazoo River was designated a Superfund site, referred to as the Kalamazoo River Area of Concern (KRAOC). The site extends from Morrow Dam in Kalamazoo County to Lake Michigan (Figure 1). The release of polychlorinated biphenyls (PCBs), the primary contaminants of potential ecological concern (COPECs), resulted from PCB-contaminated waste discharged from the recycling and processing of carbonless copy paper (1). During the period from 1957 to 1971, the ink solvent used in carbonless copy paper contained mixtures of PCBs, primarily Aroclor 1242 (2). Aroclor 1254 may also have been added to inks and other additives in lesser amounts (2). The majority of PCBs in the Kalamazoo River watershed are associated with sediment deposits in a series of impoundments. However, partial removal of three dams (e.g., Plainwell, Otsego, and Trowbridge) to their sill levels in the 1970s allowed substantial amounts of sediments to be transported downstream, lowered the water levels to the sill of the dams' spillways, and exposed former sediments in the former impoundments. Much of the exposed former sediment is within the flood plain and thus becomes periodically inundated during high flow events.

PCBs are an environmentally ubiquitous, complex mixture of individual compounds that are chlorinated with 1–10 chlorines in various combinations of positions to create a total of 209 possible congeners. Historically, site-specific PCB data from samples collected from the KRAOC have been quantified as Aroclors 1016, 1242, 1248, 1254, and/or 1260 (1). However, the analytical methodologies used in these investigations (i.e., EPA Methods 8080 and 8081) do not measure "Aroclors" but rather a pattern of PCB congeners. The analyst then determines the Aroclor pattern that most closely approximates that mixture of PCB congeners. In some cases, the PCBs were quantified as a particular Aroclor simply because that Aroclor or mixture of Aroclors was used as the standard.

Each Aroclor is a complex mixture of numerous PCB congeners, and each congener behaves independently once released to the environment. Due to selective volatilization, degradation, accumulation, sorption, and metabolism (i.e., collectively termed "environmental weathering"), the relative concentrations of congeners in a mixture or matrix change as a function of time. Limitations associated with Aroclor-based determination of PCBs in environmental samples have been recognized for a long time (3–6) and have been acknowledged by the U.S. EPA (7, 8) and the National

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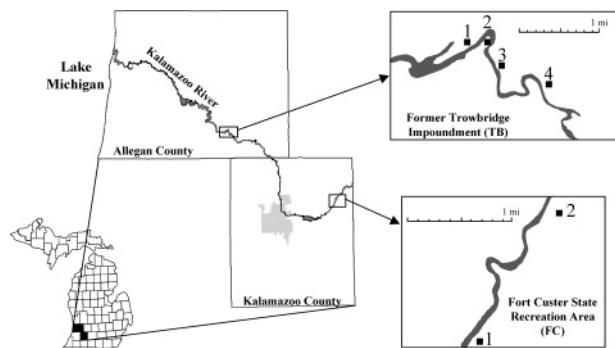


FIGURE 1. Site location map for the sampling grids at the former Trowbridge impoundment (TB) and the Fort Custer (FC) reference area along the Kalamazoo River, Michigan.

Research Council (9). In addition, there are difficulties and uncertainties with assessing the toxicity of environmentally weathered PCB mixtures that are quantified as Aroclors. Congener-specific analysis, including coplanar PCB congeners combined with a calculation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) equivalents (TEQs), is generally thought to correlate better with toxicity than measures of total PCBs (10–12). However, recent work by Custer et al. (13) calls into question whether toxic equivalency factors (TEFs) developed for PCBs are appropriate to predict effects in some bird species.

While considerable work has been conducted on the environmental fate and bioaccumulation of PCB congeners in aquatic habitats (14–16), very little is known about the environmental fate and bioaccumulation of PCB congeners in terrestrial systems. Therefore, the specific focus of the current study is the riparian, seasonally terrestrial/flood plain habitat along the Kalamazoo River. These flood plains are generally broad and covered with lowland forest or located within marshy wetlands. Specifically, wetland habitats within the Kalamazoo River watershed include marsh, wet meadow, wooded swamp, and bottomland forest. Associated water regimes range from permanently flooded for some marsh habitats to temporarily or seasonally flooded for the wet meadow and bottomland forest habitats. Wooded vegetation along the Kalamazoo River and flood plain consists of varying mixtures of willow, cottonwood, silver maple, and ash, with sycamores scattered throughout the lowland areas. Extensive wetlands along the river contain varying amounts of purple loosestrife, cattails, sedges, rushes, and aquatic species such as pond weeds and water lilies. In the former impoundments, there are large open areas dominated by *Ambrosia trifida* (giant ragweed), *Urtica dioica* (stinging nettles), *Elytrigia repens* (quack grass), *Conium maculatum* (poison hemlock), *Alliaria petiolata* (garlic mustard), and *Silica alba* (white campion). Riparian habitats along the Kalamazoo River provide food and forage for diverse species of wildlife.

These areas of intermittently flooded wetland soils have substantially different ecological functions compared to true sediments in permanently flooded areas and also have substantial differences in chemical fate, transport, bioavailability, and wildlife exposure. Delineation between soil and sediment within wetland habitats becomes arguably more difficult in such areas and based on traditional criteria may or may not coincide with a delineation that is most appropriate for the management of risk for receptors of concern. One approach for delineation can be based on the habitat it supports and other factors such as duration of water inundation, exposure potentials for key receptors, bioavailability, concentrations of PCBs, concentrations of organic matter, vegetation types, and prevalence of invertebrate type (benthic or terrestrial). Taken together, site-specific wildlife exposure data and site-specific conceptual site models

support the conclusion that key receptor exposures likely diverge at the invertebrate level within wetland habitats under the premise that terrestrial invertebrates are associated with soils and benthic invertebrates are associated with sediments.

The focus of the current investigation was the intermittently flooded wetland soils and the accumulation of PCBs in the associated terrestrial food web. The purposes of this study were to (1) determine congener-specific PCB concentrations and relative patterns of congeners in terrestrial samples collected from the Kalamazoo River flood plain, (2) compare congener concentrations and patterns spatially and temporally between locations, (3) examine and contrast congener concentrations and patterns among trophic levels to gain a better understanding of the dynamics and accumulation of PCBs in a terrestrial food web, and (4) compare the relationship between concentrations of total PCBs and TEQs across multiple levels of the terrestrial food web. The results presented here are part of a larger and more comprehensive set of field investigations that were designed to gather site-specific data on the concentrations of individual PCB congeners. Taken together, the results from these studies will better define PCB exposures by determining site-specific dietary composition of key receptors, PCB concentrations in site-specific prey items, tissue residue levels in key receptors, and data necessary to develop a food web model that can be used to address movement of PCBs within the KRAOC food web.

Experimental Section

Study Area Locations. This study focused on two locations for food web analysis. Within the KRAOC, the former Trowbridge impoundment was selected as a study site since it is the largest of the three former impoundments (e.g., containing approximately 132 hectares of former sediments and 69 hectares of existing impounded water), has the greatest mass of PCBs, and has the greatest surficial mean concentration of PCBs in soils (approximately 11 mg/kg, dry weight (dw)) relative to the other former impoundments. Within the former Trowbridge impoundment (TB), four sampling grids were established within the flood plain (Figure 1). Fort Custer State Recreation Area (FC) was selected as a reference site for this study because it is upstream of the KRAOC and is relatively uncontaminated with PCBs. Specifically, FC is about 30 miles upstream of TB. Within the reference area at FC, two sampling grids were established within the flood plain (Figure 1).

Sampling Grid Design and Collection Methods. Most samples of plants, soils, above-ground invertebrates, subterranean invertebrates (earthworms), and small mammals were collected simultaneously (within a specified sampling period) within a 30 × 30 m² sampling grid. Specifically, plants, earthworms, and colocated soils were collected from a randomly selected 1 m² area within the sampling grid. A few samples were collected in close proximity but outside of specified sampling grids based on targeted species of plants and birds. For plant collections, at least 10 g of plant material was collected above the root crown. Also, seeds and/or fruits likely to be consumed by songbirds and those plant species previously identified as PCB bioaccumulators (Dave Charters, personal communication) were targeted. Soil samples were collected using a Wildco stainless steel core sampler (2 in. diameter; 20 in. length) or a bucket auger (2 in. diameter; 6 in. length). For earthworms, two composite samples of approximately 20 g were collected from each sampling grid during every sampling event. One earthworm composite sample (termed “nondepurated”) was rinsed with water and analyzed for PCBs. The other earthworm composite sample (“depurated”) was rinsed with water and allowed to depurate for 24–48 h.

All samples were collected under approved state and federal permits and in accordance with Michigan State University's All-University Committee on Animal Use and Care. Above-ground terrestrial invertebrates were collected by hand picking and sweep nets. Invertebrates were sorted and classified into orders before analysis. Small mammals, including the white-footed deer mouse (*Peromyscus leucopus*), red squirrel (*Tamiasciurus hudsonicus*), Eastern chipmunk (*Tamias striatus*), meadow jumping mouse (*Zapus hudsonicus*), meadow vole (*Microtus pennsylvanicus*), short-tailed shrew (*Blarina brevicauda*), and masked shrew (*Sorex cinereus*) were collected by setting 49 alternating Sherman live traps and pitfall traps that were placed within each sampling grid. Eggs and nestlings of house wren (*Troglodytes aedon*) and Eastern bluebird (*Sialia sialis*) were collected from nest boxes within the study areas. Adult house wrens and American robins (*Turdus migratorius*) were collected by either mist-netting or gunshot (17–18). Addled eggs and plasma from great horned owls (*Bubo virginianus*) were collected from natural nests or artificial nesting platforms within the TB and FC study areas.

Sampling Rounds. Samples were collected during the years of 2000, 2001, and 2002, with most samples being collected during 2000 and 2001. To address seasonal trends in concentrations of PCBs, samples were collected during distinct spans of time or “periods” during the spring and summer of 2000. Time periods for sample collections were as follows: period 1 for soils, plants, terrestrial invertebrates, and earthworms, May 22–June 21, 2000; period 2 for soils, plants, terrestrial invertebrates, and earthworms, July 17–Aug 16, 2000; period 3 for soils, plants, terrestrial invertebrates, and earthworms, Aug 24–Sept 19, 2000; period 1 for small mammals and shrews, June 7–July 20, 2000; period 2 for small mammals and shrews, Aug 26–Sept 19, 2000.

Analytical Methodology. Surrogate standards, PCB 204 (IUPAC) and PCB 30 (AccuStandard, New Haven, CT), were added to all samples, blanks, and matrix spikes before Soxhlet extraction. Each analytical batch consisted of 20 samples, at least one extraction blank, a matrix spike and matrix spike duplicate, laboratory spike, and standard reference material. PCBs including di- and mono-ortho-substituted congeners were quantified by use of a gas chromatograph (Perkin-Elmer AutoSystem) equipped with a J&W DB-5 30-m capillary column and a ^{63}Ni electron capture detector (GC-ECD). A solution containing 98 individual PCB congeners with known composition and content was used as a standard. Congeners were identified by comparing sample peak retention times to those of the known standard. In sample extracts, concentrations of each congener were determined by comparing the peak area to that of the appropriate peak in the standard mixture after an initial five-point calibration assured instrument linearity. PCB congeners were quantified by use of a gas chromatograph (Perkin-Elmer AutoSystem or Hewlett-Packard 5890 SII) equipped with a ^{63}Ni electron capture detector. Concentrations of all resolved PCB congeners were summed to obtain total PCB concentrations. The concentrations of the surrogate standards were calculated and used to determine extraction efficiency for each sample. A conservative estimate of the method detection limit for individual congeners is 1 ppt. This method detection limit is based on the injection volume of 1 μL , the signal-to-noise ratio of a 25 ppt standard, and the mass of sample extracted.

Non-ortho-substituted (coplanar) PCB congeners 77, 81, 126, and 169 were separated from coeluting congeners and interferences by cleanup on a carbon-impregnated silica gel column. Extracts were analyzed by GC-MS on a Hewlett-Packard 5890 series II gas chromatograph equipped with a Phenomenex ZB-5 30-m capillary column and a HP 5972 series mass-selective detector. Non-ortho-substituted PCB congeners were detected and confirmed by selected ion

monitoring of the two largest ions of the molecular cluster. Congener concentrations were calculated based on ion ratios for the native and ^{13}C congener.

Calculation of TCDD Equivalents. Concentrations of TEQs in samples were calculated by multiplying the concentration of individual PCB congeners by its respective World Health Organization (WHO) toxic equivalency factor (TEF) (19). Total TEQ concentrations were determined by summing the concentrations of the TEQs of congener IUPAC numbers 77, 81, 105, 118, 126, 156, 157, 167, and 169. When a congener was not detected, a surrogate value of one-half of the limit of detection was multiplied by the TEF to calculate the congener-specific TEQ. The potential impact of assigning a proxy value of one-half the detection limit for the TEQ calculations was found to be minimal for samples from Trowbridge (data not shown). To test this, a ratio was calculated between the maximum estimated TEQ concentration (using the full detection limit for congeners that were not detected) and the minimum estimated TEQ concentration (using a value of zero for congeners that were not detected). As expected, with samples from Fort Custer, there was more uncertainty in the estimated TEQ concentrations as there were more congeners that were not detected. Due to the differing sensitivities of mammals, birds, and fish toward PCBs and other dioxin-like chemicals, three sets of TEF values have been developed for TEQ calculations that apply to mammalian, avian, and fish receptor species (19). When mono-ortho congeners coeluted with other PCB congeners, the total concentration for that coeluting pair was considered to be entirely due to the mono-ortho congener. Thus, for a sample with coeluting congeners, the TEQ concentration was overestimated.

Statistical Analysis. The Kolmogorov–Smirnov one-sample test with Lillifor's transformation was used to assess whether total PCB data sets were normally distributed. When data were normally distributed, analysis of variance (ANOVA) followed by Tukey's honestly significant difference (HSD) was used to detect significant differences among data sets (20). When data sets were not normally distributed, the nonparametric Kruskal–Wallis test was used to detect differences among data sets. When total PCBs between the TB and the FC locations were compared, the two-group t-test or the Mann–Whitney U-test was used if the data was normally distributed or nonnormally distributed, respectively. The criterion for significance that was used in all statistical tests was $p < 0.05$.

Results and Discussion

Ranges of PCB and TEQ Concentrations in Terrestrial Food Web Components. Concentrations of total PCBs and TEQs were significantly greater in terrestrial food web components from TB in the KRAOC than those from the upstream reference site at FC (Tables 1 and 2). Maximum observed concentrations were 36.3 mg/kg wet weight (ww) in a single house wren egg from TB and 0.47 mg/kg (ww) in a single great horned owl egg from FC. For avian TEQs, the maximum observed concentrations were 5500 ng/kg (dw) in soil at TB and 49 ng/kg (ww) in a shrew from FC. Average concentrations of total PCBs in soils from TB were approximately 700-fold greater than those of soils from the reference site. However, average concentrations of total PCBs in orthoptera (i.e., crickets and grasshoppers), plants, and small mammals (excluding shrews) from TB were only approximately 2-, 7-, and 6-fold greater than those of the reference area, respectively. Taken together, these data suggest that plants do not readily bioaccumulate PCBs from soil and that exposure to PCBs via soil and plant ingestion is likely minimal to herbivores relative to carnivores (discussed below). Some of the plants that were collected included those previously characterized as PCB bioaccumulator species such as grasses,

TABLE 1. Total PCB Concentrations (mg/kg, ww) in Soil and Soil-Associated Biota from the Former Trowbridge Impoundment (TB) and the Fort Custer State Recreational Area Reference Site (FC)

	TB location				FC location			
	N	mean % lipid ^a	mean total PCBs (mg/kg) ^b	geometric mean (mg/kg) ^b	N	mean % lipid ^a	mean total PCBs (mg/kg) ^b	geometric mean (mg/kg) ^b
soil ^a	21	5.4	6.5 ± 4.7 ^e	4.7	8	4.9	0.009 ± 0.009	0.005
plants	28	0.70	0.023 ± 0.044 ^e	0.009	10	3.0	0.003 ± 0.003	0.002
terrestrial invertebrates ^c	30	5.6	0.34 ± 0.57 ^e	0.10	18	4.2	0.023 ± 0.032	0.007
fresh earthworms	18	2.0	1.7 ± 1.8 ^e	1.1	9	1.9	0.003 ± 0.001	0.002
depurated earthworms	14	2.2	1.3 ± 1.1 ^e	0.86	7	1.8	0.006 ± 0.004	0.005
small mammals ^d	21	4.8	0.13 ± 0.16 ^e	0.074	18	4.1	0.021 ± 0.042	0.007
shrews	17	2.9	1.3 ± 0.94 ^e	0.85	16	4.2	0.009 ± 0.005	0.008
house wren eggs	21	10	8.2 ± 8.3 ^e	5.8	15	13	0.12 ± 0.12	0.067
house wren nestlings	18	6.1	1.4 ± 2.7 ^e	0.70	13	5.3	0.020 ± 0.020	0.015
house wren adults	9	5.4	3.2 ± 2.0 ^e	2.6	8	4.6	0.072 ± 0.032	0.064
bluebird eggs	10	9.6	7.4 ± 5.3 ^e	5.2	15	8.1	0.16 ± 0.10	0.13
bluebird nestlings	7	4.5	1.7 ± 2.33 ^e	0.72	19	4.8	0.015 ± 0.013	0.012
American robin adults	17	4.3	0.92 ± 1.2 ^e	0.30	4	2.3	0.091 ± 0.15	0.030
great horned owl plasma	7	0.49	0.045 ± 0.022	0.040	1	0.46	0.008	0.008
great horned owl eggs	4	7.2	1.6 ± 0.87	1.4	1	5.8	0.47	0.47

^a Mean percent organic carbon reported for soils; mean ± standard deviation. ^b Concentrations of total PCBs (mg/kg, wet weight basis for biota and dry weight basis for soils) based on PCB congeners as described in text. ^c Earthworms were treated separately from other terrestrial invertebrates. ^d Shrews were treated separately from other small mammals. ^e Indicates a significant difference from the FC reference site at $p < 0.05$.

TABLE 2. Average Concentrations of Avian and Mammalian TEQs among Various Trophic Levels in the Terrestrial Food Web at Both the Former Trowbridge Impoundment (TB) and the Fort Custer State Recreational Area Reference Site (FC)

	TB location					FC location				
	N	avian TEQs (ng/kg) ^a		mammalian TEQs (ng/kg) ^a		N	avian TEQs (ng/kg) ^a		mammalian TEQs (ng/kg) ^a	
		mean	geometric mean	mean	geometric mean		mean	geometric mean	mean	geometric mean
soil	21	1240 ± 1410 ^d	303	77 ± 50 ^d	55	8	0.79 ± 0.73	0.42	0.40 ± 0.49	0.24
terrestrial invertebrates ^b	30	80 ± 200 ^d	12	7.5 ± 12 ^d		18	1.6 ± 2.0	0.34	0.61 ± 0.74	
fresh earthworms	18	238 ± 255 ^d	117	13 ± 8.1 ^d	3.0	9	0.65 ± 0.48	0.54	0.41 ± 0.37	0.18
depurated earthworms	14	154 ± 186 ^d	93	10 ± 9.5 ^d	10	7	1.8 ± 4.0	0.47	1.1 ± 2.4	0.31
small mammals ^c	21	9.8 ± 19 ^d	4.6	9.4 ± 20 ^d	7.2	18	0.89 ± 1.0	0.58	0.70 ± 0.90	0.29
shrews	17	72 ± 69 ^d	47	60 ± 56 ^d	4.0	16	4.2 ± 12	1.3	3.7 ± 12	0.41
house wren eggs	21	423 ± 587 ^d	250	<i>e</i>	<i>e</i>	15	6.0 ± 4.5	0.94	<i>e</i>	<i>e</i>
house wren nestlings	18	89 ± 117 ^d	58	<i>e</i>	<i>e</i>	13	1.4 ± 0.96	1.2	<i>e</i>	<i>e</i>
house wren adults	9	107 ± 57 ^d	91	<i>e</i>	<i>e</i>	8	7.1 ± 5.7	5.8	<i>e</i>	<i>e</i>
bluebird eggs	10	57 ± 60 ^d	38	<i>e</i>	<i>e</i>	15	2.9 ± 4.7	1.3	<i>e</i>	<i>e</i>
bluebird nestlings	7	6.7 ± 4.7 ^d	5.3	<i>e</i>	<i>e</i>	19	1.6 ± 1.3	1.3	<i>e</i>	<i>e</i>
American robin adults	17	3.9 ± 4.4	2.4	<i>e</i>	<i>e</i>	4	1.1 ± 0.55	0.96	<i>e</i>	<i>e</i>
great horned owl plasma	2	0.69 ± 0.79	1.6	<i>e</i>	<i>e</i>	1	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
great horned owl eggs	4	13 ± 10	11	<i>e</i>	<i>e</i>	1	8.4	8.4	<i>e</i>	<i>e</i>

^a Concentrations of TEQs (ng/kg, wet weight basis for biota and dry weight basis for soils) based on PCB congeners as described in text; mean ± standard deviation. ^b Earthworms were treated separately from other terrestrial invertebrates. ^c Shrews were treated separately from other small mammals. ^d Indicates a significant difference from the FC reference site at $p < 0.05$. ^e Not calculated.

quackgrass, sumac, and aspen (Dave Charters, personal communication). However, in this study, there were no statistically significant differences in concentrations of total PCBs among these bioaccumulating species and any other plant samples that were analyzed.

Average concentrations of PCBs in coleoptera (i.e., beetles), house wren eggs, shrews, and depurated earthworms were approximately 50-, 70-, 150-, and 200-fold greater at Trowbridge than those from the reference area, respectively. The coleoptera samples included a considerable quantity of June bugs (*Phyllophaga* sp.) and Japanese beetles (*Popillia japonica*), the larval stage of which resides in soil as grubs. In addition, the larval stages of some coleopteran species are very rich in lipids (21), which combined with the contact with soil during this life stage may account for the greater accumulation of PCBs in coleopteran species as compared to that in orthopteran species, which are not as closely linked to the soil environment.

As no reports could be found in the literature comparing PCB uptake between fresh and depurated earthworms,

concentrations of PCBs were compared in samples matched for the same sampling grid and time point. While variable and not statistically significant, the concentrations of PCBs at the TB sampling area tended to be greater in the fresh earthworms compared to those of depurated earthworms, whereas at Fort Custer concentrations of PCBs were all less in the fresh earthworms than the depurated earthworms (data not shown). At each sampling area, the relationship was found to be poor between concentrations of PCBs in soil (on a dry weight or organic-carbon-normalized basis) and fresh or depurated earthworms (on a wet weight or lipid-normalized basis; data not shown).

Due to its relatively great ingestion rate, relatively small home range (varies from 0.39 to 0.96 ha (22–23)), and its relatively short lifespan (approximately 1 year (24–25)), the short-tailed shrew has been recommended as a sentinel species of contaminant exposure based on trophic level and value as a bioindicator (26). At TB, shrews tended to have approximately 10-fold greater concentrations of total PCBs than other small mammals, such as white-footed mice, moles,

TABLE 3. Bioaccumulation Factors of Total PCBs (Organic-Carbon- and Lipid-Normalized) among the Terrestrial Food Web at the Former Trowbridge Impoundment (TB) and the Fort Custer State Recreational Area Reference Site(FC)^a

trophic transfer	TB location	FC location
Biota–Soil Accumulation Factor (BSAF)		
soil → terrestrial plant	0.016	2.5
soil → terrestrial invertebrates ^b	0.022	2.0
soil → earthworms (nondepurated)	0.66	0.99
soil → earthworms (depurated)	0.48	2.4
soil → small mammals	0.018	1.6
soil → shrews	0.35	1.6
soil → robin adults	0.080	10
soil → house wren eggs	0.76	6.1
soil → bluebird eggs	0.74	13
soil → great horned owl eggs	0.23	64
Biomagnification Factor (BMF)		
plant → small mammals	1.1	0.65
terrestrial invertebrates ^b → shrews	16	0.83
earthworms (depurated) → shrews	0.74	0.69
earthworms (depurated) → robin adults	0.17	4.4
terrestrial invertebrates ^b → house wren eggs	35	3.1
terrestrial invertebrates ^b → bluebird eggs	34	6.6
small mammals → great horned owl eggs	13	40

^a Biomagnification calculations were made based on the assumption that total PCB concentrations in soils and biota and bioavailability of PCBs were homogeneous throughout each location. Animal data were normalized by lipid content, while soil data were normalized by organic carbon content. Calculations were based on geometric means. ^b Earthworms were treated separately from other terrestrial invertebrates.

and voles. This trend has been observed with other persistent, bioaccumulative compounds such as dichlorodiphenyl-trichloroethane (DDT) (27). Thus, these data support the selection of the short-tailed shrew and similar species as ecological receptors of concern due to their relatively great potential for exposure relative to other terrestrial mammalian species.

When data for individual sampling grids within each location were compared, there were no statistically significant differences in concentrations of PCBs or TEQs among sampling grids within either the TB or the FC sampling areas (data not shown). In addition, there were no statistically significant temporal differences.

Bioavailability and Bioaccumulation. Except for eggs of house wrens and Eastern bluebirds, average concentrations of total PCBs in all food web items from TB were less than the average concentration of total PCBs in soil. When PCB concentrations were normalized to organic carbon for soils and lipids for biota, the accumulation of PCBs from soil (defined as the biota–soil accumulation factor or BSAF) was less than unity for all of the TB sample types (Table 3). Limited evidence suggests that bioavailability decreases over time as chemicals age in soil (28). This may be due in part to the relatively great binding affinity of many PCB congeners to particulate matter and the diffusion of PCB congeners into the soil lattice and Donnan spaces. Also, at TB, concentrations of total organic carbon in flood plain soils (with an average of approximately 5–6%) may further reduce bioavailability of PCBs. On the basis of available life history information, most of the target biota at TB would be expected to reside and forage within the contaminated flood plain. However, some of the species may not be year-round residents (e.g., passerine species). Thus, there is some uncertainty regarding what their exposures might be when these species are not at TB. The slightly greater concentrations of PCBs in passerine bird eggs compared to other sample types are likely due to a 13–15-fold biomagnification from terrestrial invertebrates (Table 3). Similar trophic-transfer biomagnification factors (BMFs) of approximately 8–10-fold were observed for insects

to shrews and small mammals to great horned owls. While it should be noted that these are apparent BMFs since the actual diet is unknown, these data demonstrate the potential for biomagnification of PCBs in a terrestrial food web. Similar observations have been made for simple terrestrial food webs (29–31). The BSAF for earthworms at Trowbridge is similar to that observed for earthworms in the Rhine Delta flood plains, whereas the BSAF for shrews at Trowbridge is lower than those from the Rhine Delta flood plains (31).

However, in areas where PCB concentrations in soil are relatively low, such as with the FC reference area, PCB concentrations in some biota samples were greater than the concentrations in soil. In addition, the BSAFs for Fort Custer were greater than unity for several matrixes. In part, this may be due to a relatively greater influence of atmospheric input and other potential exposure pathways at the reference area. Alternatively, it may be possible that there are concentration-dependent differences in the efficiency of biota to uptake PCBs from soil. Taken together, these observations demonstrate that caution should be exercised when applying BSAFs across sites with greatly different PCB concentrations. Similar cautions have been raised in regards to the application of BSAFs from one site to another since there are potential differences in soil and sediment characteristics that may affect bioavailability (32).

PCB Congener Composition in Terrestrial Food Web Components. If differential environmental weathering of PCB congeners did not occur, then one might expect somewhat similar patterns of PCB congeners between soil and components of the terrestrial food web. However, there were clear qualitative differences (discussed in detail below) in the patterns of relative PCB congener concentrations in most components of the food web compared to that of soil (Figure 2). Exceptions to this generality included earthworms and coleoptera composite samples, which exhibited remarkably similar PCB congener patterns to collocated soils (Figure 2). As discussed earlier, the coleoptera samples included a considerable quantity of June bugs (*Phyllophaga* sp.) and Japanese beetles (*Popillia japonica*), the larval stage of which reside in soil as grubs. The intimate contact with soil for earthworms and the larval stages of the coleoptera samples coupled with their relative inability to metabolize PCBs are likely factors to explain the similar congener patterns that were observed.

For most of the other food web components, the PCB congener patterns were dramatically different from that of soils. In plants, for example, there was a marked shift toward lesser chlorinated congeners with a marked decrease in more chlorinated congeners. Taken together with the very low concentrations of total PCBs in plants relative to soil, these data are consistent with the fact that PCBs are not readily translocated into above-ground plant tissue. While it is possible that some of the PCBs in the plant tissue could be due to deposition of PCB-containing silt and particulates during times of inundation, the most likely mechanism is aerial deposition of lighter, more volatile congeners followed by absorption in the waxy cuticle (33).

For shrews, there was a dramatic shift in PCB patterns compared to that of soil (Figure 3). The lesser chlorinated PCB congeners were noticeably diminished whereas there was a notable enrichment of PCBs 153, 180, 138, 118, and 99. A similar pattern was observed for small mammals excluding shrews (data not shown) and passerine samples, indicating that this phenomenon may occur with a diverse array of species, at least those species with a functional Ah-receptor-mediated pathway leading to inducible cytochrome P450 enzyme activity and therefore greater metabolic capabilities.

One way to evaluate the potential role of metabolism on the relative differences in congener patterns in a food web is to group PCB congeners by structural features that are

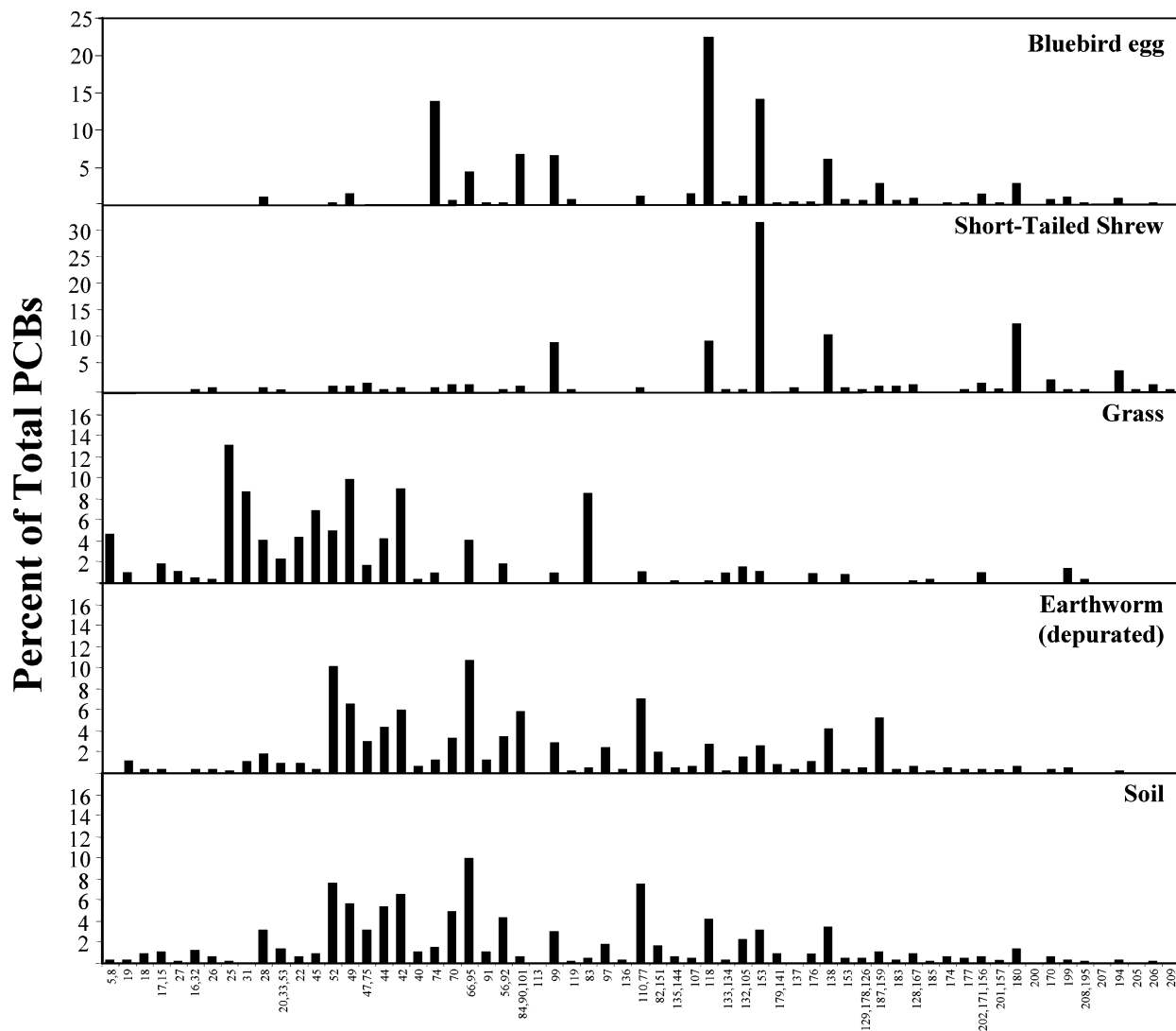


FIGURE 2. PCB congener pattern for representative samples of soil, grass, depurated earthworm, short-tailed shrews, and bluebird eggs collected from the former Trowbridge impoundment. Data (expressed as a weight percent relative to total PCBs) are from Trowbridge grid 1 in 2000.

related to potential susceptibility to catabolic metabolism (34–35). For example, many species of vertebrates are capable of enzymatically modifying congeners with adjacent unsubstituted meta and para carbons (i.e., lacking chlorines in these positions). Some species, including some marine mammals, can also enzymatically modify congeners with adjacent unsubstituted ortho and meta carbons (36). Such congeners can potentially be hydroxylated and excreted. If one evaluates the ratio of congener concentrations in earthworms from Trowbridge to that of colocated soil, often termed the biota–soil accumulation factor (BSAF), the ratio for the most abundant congeners ranged from 0.2 to 0.7, regardless of ortho-, meta-, and para-substitution patterns, with the exception of the coeluting pair of PCB 159/187 (Figure 3). In contrast, there were considerable differences in BSAFs among congeners for shrews. For example, average concentrations of PCB congeners with adjacent unsubstituted meta and para carbons (groups C and D in Figure 3) were diminished in shrews relative to soils, whereas congeners were generally stable or enriched with no adjacent unsubstituted meta and para sites (groups A and B in Figure 3). Thus, shrews, which occupy trophic positions higher up on the food chain and have relatively great metabolic capacity, appear capable of metabolizing certain congeners (e.g., generally those with adjacent unsubstituted meta and para carbons). This has been shown previously in aquatic systems

and selected terrestrial species (34, 36–37), but to our knowledge this has not been demonstrated in a complex terrestrial food web.

In general, it is not valid to apply a BSAF or BMF to transfer TEQs from one trophic level to another. This is because TEQs include a fractional contribution from several congeners that have unique toxicokinetic profiles. For this reason, each individual PCB congener needs to be corrected not only for its relative toxic potency but also its accumulation potential. In particular, PCB congeners 77 and 81, which may account for a substantial portion of the predicted avian TEQ concentration, are much more susceptible to metabolism than other congeners such as PCB congeners 126 and 169 (11, 37–39). Even when such toxicokinetic differences are accounted for, there remains additional uncertainty regarding WHO avian TEFs. Recent work by Custer et al. (13) calls into question whether TEFs developed for PCBs are appropriate to predict effects in birds. For example, on the basis of tree swallow studies on the Woonasquatucket River, Custer et al. (13) derived a LD₅₀ concentration of 1700 pg/g of TEQs in field-collected tree swallow eggs (primarily due to TCDD). However, if one compares this LD₅₀ to concentrations of TEQs (calculated from PCBs) between 1730 and 12700 pg/g ww in tree swallow eggs from the Hudson River, then one would expect considerable population-level effects due to mortality. However, there were minimal effects on subtle endpoints at

Example structure for each grouping:

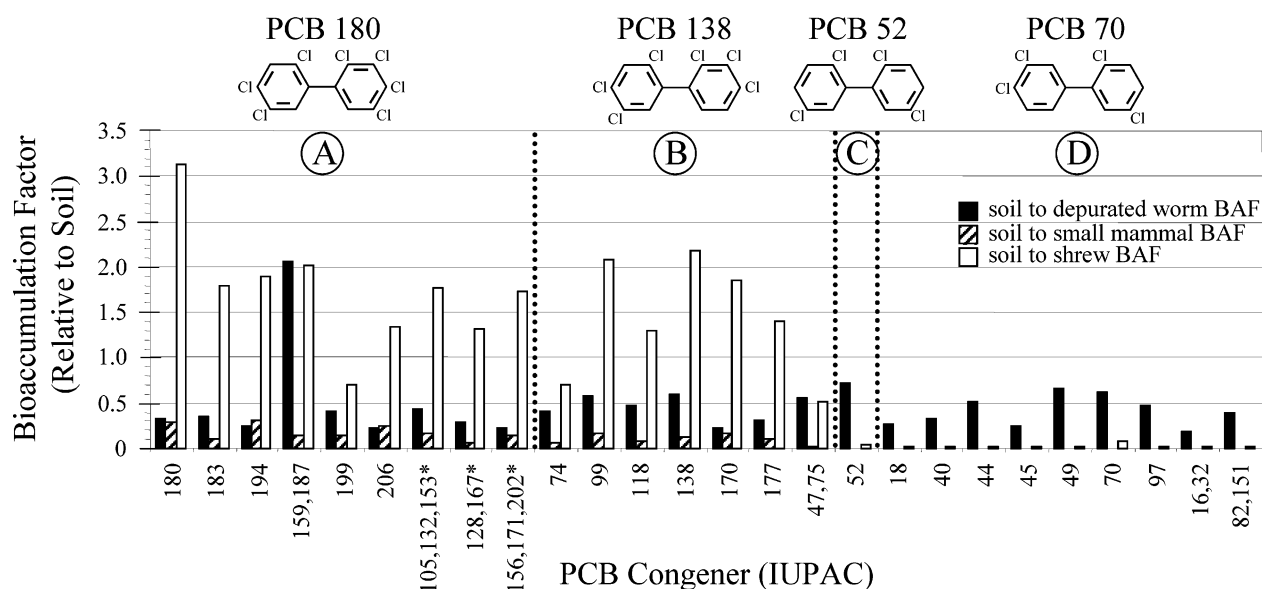


FIGURE 3. Relative accumulation of PCB congeners from soil to earthworms, shrews, and small mammals (excluding shrews) from the former Trowbridge impoundment (TB). Average PCB congener concentrations were adjusted to organic carbon content in soil and percent lipid in biota. PCB congeners are grouped as follows based on structural similarities: group A, no adjacent unsubstituted ortho–meta or meta–para sites; group B, adjacent unsubstituted ortho–meta but not meta–para sites; group C, adjacent unsubstituted meta–para but not ortho–meta sites; group D, adjacent unsubstituted ortho–meta and meta–para sites. The asterisk indicates that these coeluting congeners include congeners from both group A and group B.

TEQ concentrations (based on PCBs) in tree swallow eggs from the Hudson River (40). In other words, on the basis of this one comparison, a concentration of TCDD may not be toxicologically equivalent to the same concentration expressed as TEQs calculated from avian TEFs when PCBs contribute substantially to the calculated TEQs.

The relative potency of a PCB congener mixture can be calculated by dividing the concentration of TEQs (ng TEQs/kg) by the concentration of PCBs (mg PCBs/kg) in the same sample. The ratio of such relative potencies among different trophic levels is a useful measure of how the relative potency changes at each trophic level (38). Taken together with the BMF for total PCBs, a holistic picture can be developed that shows how both total PCB concentrations and dioxin-like potency of the PCB congener mixture changes by trophic level (Figure 4). From this analysis, it is clear that at TB there is a general reduction of relative potency (e.g., less than unity) at most trophic levels regardless of whether PCBs are biomagnified or not. For example, there is an apparent biomagnification of total PCBs going from terrestrial invertebrates to shrews (BMF = 16) whereas the relative potency ratio is only 0.23. For this example, the reduction in relative potency in shrews is, in part, due to lower concentrations of PCB 77, a congener that has been found to be susceptible to metabolism (11). One exception was for soil to terrestrial invertebrates, which is understandable since terrestrial invertebrates have a relatively low metabolic capacity. Another exception was the trophic transfer from adult robins to great horned owl eggs, in which there was an increase in both relative potency and in total PCB concentration. Since it is unclear how much of the great horned owl diet may consist of robins and similar passerine species, this apparent BMF may be an artifact. Also, since great horned owl samples are more limited in number and difficult to obtain compared to other sample types, the conclusions that have been drawn for this sample type are relatively limited.

Finally, in ecological risk assessments there is often a desire to predict concentrations of TEQs from total PCB data. This desire stems from the general thought that toxicity is better

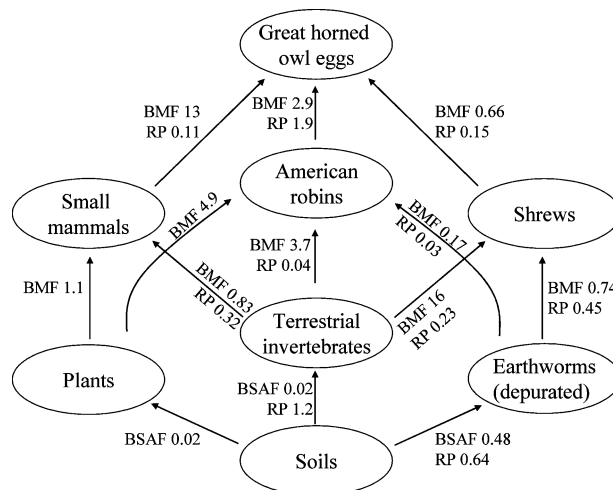


FIGURE 4. Lipid-normalized biota–soil accumulation factors (BSAFs), biomagnification factors (BMFs), and relative potency ratios (RPs) of the PCB congener mixtures at each trophic level using data from the former Trowbridge impoundment (TB).

correlated to TEQs than PCBs. However, there is often a lack of appropriate congener-specific data due to cost or other constraints at PCB-contaminated sites. EPA guidance suggests that for a given site it may be cost-effective and appropriate to analyze a subset of site-related samples for both total PCBs and PCB congeners to derive a correlation from which concentrations of TEQs may be estimated (8). Therefore, we evaluated the relationship between concentrations of PCBs and avian TEQs. While there was a general trend, as expected, in which concentrations of TEQs increased with total PCBs, this relationship was rather poor ($R^2 = 0.13$ using samples from TB and $R^2 = 0.059$ using samples from FC) when evaluated across all sample types. If one restricts the comparison among discrete sample types (using data from TB), then the correlation improves somewhat for certain sample types such as passerine adults ($R^2 = 0.50$), small

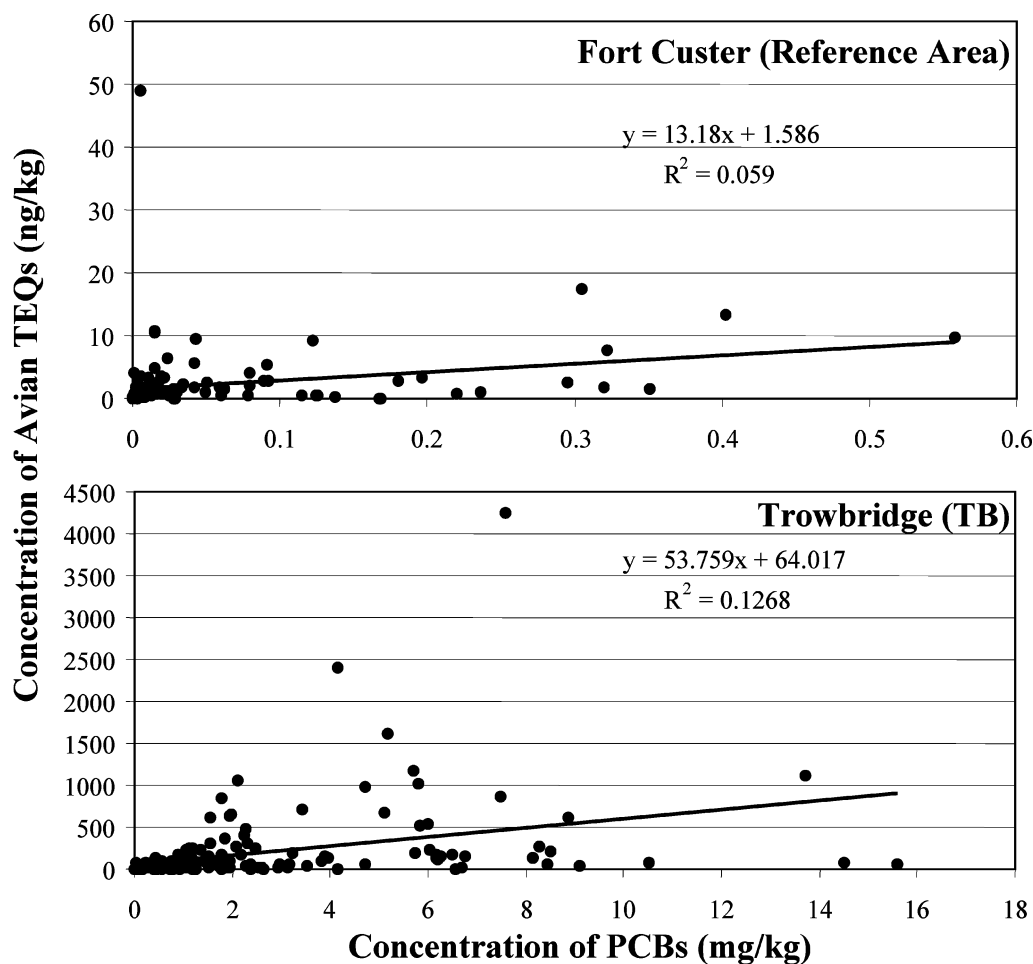


FIGURE 5. Scatter plot of PCB and avian TEQ concentrations for all individual samples from Fort Custer (top panel, 131 samples) and the former Trowbridge impoundment (lower panel, 173 samples). Concentrations are based on dry weight for soils and wet weight for biota.

mammals ($R^2 = 0.40$), terrestrial invertebrates ($R^2 = 0.49$), and worms ($R^2 = 0.42$), but the correlation was relatively poor for sample types such as soil ($R^2 = 0.16$), shrews ($R^2 = 0.0012$), and passerine nestlings ($R^2 = 0.0024$) and eggs ($R^2 = 0.0077$). Therefore, any attempts to estimate concentrations of TEQs from total PCB data should be evaluated carefully on a sample-specific basis.

On the basis of these results, if it is necessary to understand the concentration of TEQs at a site in a given sample type, then the most technically defensible approach would be to simply quantify individual PCB congeners. This would reduce uncertainty relative to estimating TEQ concentrations from total PCB data. However, the reduction in uncertainty would have to be weighed along with considerations of budgetary constraints, data quality objectives, and risk management options. Depending on the intended use of the data (e.g., delineation of the nature and extent of contamination, source evaluation, exposure assessment, and/or risk characterization), several factors should be evaluated to balance needs for information gained from congener-specific PCB analysis relative to uncertainty reduction and cost-effectiveness. For example, in the cases of nature and extent evaluation and screening-level ecological risk assessments, there may be little need to conduct congener-specific analysis when total PCB quantification can be conducted at a fraction of the cost and be sufficient to achieve the objectives. However, if there are multiple PCB sources that may need to be evaluated or if there is a relatively great likelihood of wildlife exposure, then congener-specific analysis of at least a subset of samples would be advisable. On the basis of the analyses of how well (or poorly) concentrations of TEQs relate to concentrations

of total PCBs, it may be advisable to analyze all wildlife samples with congener-specific analysis. Finally, in the case of relatively rare samples of certain receptor tissues (e.g., peregrine falcon eggs, etc.), it is highly recommended that a congener-specific analysis with ultralow detection limits for coplanar PCB congeners be performed to maximize the information gained from such a limited sample.

In conclusion, concentrations of PCBs were lower in biota than those in soil from the KRAOC although there was a modest biomagnification of PCBs from certain lower trophic level biota to higher trophic levels (e.g., terrestrial invertebrates to shrews, small mammals to great horned owls, etc.). Furthermore, environmental weathering of PCBs in the terrestrial food web of the KRAOC led to a decrease in the relative potency of PCBs (expressed as mg TEQs/kg PCBs) from soil to most biota. Taken together, these data suggest that differential accumulation of PCB congeners in the terrestrial food web can be explained by congener-specific differences in bioavailability from soil, exposure pathways, and metabolic potential of each of the food web components.

Acknowledgments

Funding was provided through a grant from the Kalamazoo River Study Group to Michigan State University. We thank Ryan Holem, Carrie Ruppert, George Klemolin, Pamela Moseley, and Monica Macarroll for their assistance in the field collections and Karen Smyth and Melissa Shotwell for their assistance preparing this manuscript.

Supporting Information Available

Congener-specific data for the Trowbridge and Fort Custer sites (all grids combined). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review October 28, 2004. Revised manuscript received May 23, 2005. Accepted June 8, 2005.

ES0483185

Supplemental Data Table for Fort Custer (Terrestrial Food Web)

Type and Sample size (n)	Soil (n=8)		Plants (n=10)		Ter. Inverts. (n=16)		Fresh Earthworms (n=9)		Deputed Earthworms (n=7)		Small Mammals (n=18)		Shrews (n=16)		House Wren Eggs (n=15)		House Wren Nestlings (n=13)		House Wren Adults (n=8)	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Lipid or TOC (%)	4.93	4.22	3.05	6.58	4.17	2.79	1.88	0.318	1.79	0.192	4.08	1.95	4.25	2.25	13	13.7	5.33	2.32	4.6	0.927
Total PCBs (mg/kg)	0.00907	0.00922	0.00331	0.00298	0.0233	0.0324	0.0025	0.000966	0.00611	0.00404	0.0206	0.0419	0.0089	0.00464	0.118	0.117	0.0203	0.0202	0.0716	0.0329
Total PCBs (pg/g)	9070	9220	3310	2980	23300	32400	2500	960	6110	4040	20600	41900	8900	4640	118000	117000	20300	20200	71600	32900
PCB Congener																				
4, 10	1120	1940	329	372	3990	4680	481	338	791	1120	11000	11600	326	INT	1	0	INT	INT	INT	INT
5, 8	168	254	184	251	3.06	8.72	17.2	48.7	80	100	660	832	348	242	186	718	39.5	139	156	239
6	122	168	2.63	4.6	3440	7290	58.6	173	334	541	1650	2960	358	512	9910	20100	45.5	161	641	1280
9	105	241	7.33	11	261	606	73.6	93.2	163	229	3690	8240	71.5	99.7	1	0	265	363	289	233
15,17	7.6	17	7.3	19.9	4580	13000	12.9	35.7	17	41.2	35.2	83.7	232	336	1	0	2600	4390	1	0
16,32	47.2	106	13.7	22.5	23.8	96.9	15.1	40	62	150	1	0	124	188	1	0	1	0	1	0
18	308	545	399	1130	879	2680	40.7	78.8	1	0	3.64	9.89	95.9	200	1	0	1130	4080	1	0
19	49.6	77	50.9	55.9	183	444	1	0	11	26.8	3710	14000	28.3	77.2	297	1150	777	1420	60.6	84.1
20,33,53	180	227	76.9	110	1	0	52.9	137	40	48.3	741	2900	87	111	232	893	1	0	140	263
22	2.84	4	37.4	37.4	875	2440	13.9	38.7	83	92.9	108	255	158	299	1	0	1	0	1	0
25	50	96	37	60.1	64.5	238	62.3	123	243	325	398	1640	11.7	41.6	1	0	224	332	207	332
26	51.8	112	65.9	93.3	184	561	1	0	42	108	2020	2170	91.5	122	6100	14900	177	326	267	703
27	1090	1550	29.4	58.8	4.44	10.3	1	0	150	295	43.3	106	36.6	116	1	0	1	0	72.5	202
28,31	206	290	55.8	53.5	24.6	61.4	24.7	34.4	428	549	14.2	34.0	25.2	53.7	2	0	2	0	649	879
37,41,42	206	248	146	145	76.8	318	21.7	59.4	94	235	20.4	56.2	96.2	139	306	180	2	0	288	808
40	21.9	38	55.7	145	106	445	1	0	1	0	2	41.2	312	419	1	0	1	0	1	0
44	108	152	30.9	52	663	2360	33.3	59.3	70	97	206	588	108	243	5120	19800	172	311	117	328
45	73	127	80	64.3	1070	3180	1	0	17	26.6	227	892	32.4	46.3	497	1400	47.3	116	13.4	35
47,75	2230	5700	26.3	29.7	193	353	177	266	490	440	1880	4620	48.3	94.5	5700	14000	124	326	530	529
49	113	178	28.8	37.7	2.11	4.71	12.1	31.5	89	88.7	99.7	209	138	180	1	0	142	510	73.1	124
52	126	236	40.3	84.6	37.5	100	15.9	42.1	116	116	29.6	54.7	204	294	1	0	1	0	21	52.9
56,92,84,90,101,113	253	300	211	188	120	322	137	92.1	553	610	476	773	1050	862	4.8	0.775	46.5	116	897	585
66,95,96	263	335	56.5	63.1	107	224	53	99.9	199	257	496	1670	71	174	1	0	92.4	175	849	810
70	137	202	132	86.6	245	973	29.1	44.5	364	599	2900	3360	178	1	0	757	917	468	1150	
74	13.8	23	36.9	52.9	112	348	56.4	61.8	221	226	377	868	14.2	31.8	1	0	486	750	468	1000
77, 85, 110, 120	242	251	319	611	847	2680	140	86.7	330	380	9.25	22.8	25.4	54.3	20000	43700	2870	6430	8500	14600
81,87,117	58.3	27.9	27.6	1	0	INT	94	186	94	186	72.1	301	56.8	74.9	1	0	21.1	72.4	150	141
82, 151	5.36	11	9.2	13	574	1570	32	41.2	68	148	3.06	4.48	11.9	21.4	989	2190	2	0	98.1	273
83	8.69	12	23.5	37.7	51	212	28.4	42.1	78	114	161	328	51.3	58.5	1	0	18.4	62.7	1	0
91	27.5	37	1.5	1.58	1	0	8.44	22.3	44	63.5	4.27	12.7	54.3	134	1	0	1	0	13.4	35
97	22.7	46	28.9	52.9	2.33	5.66	21.4	29.3	159	103	1	0	56.1	157	1	0	1	0	1	0
99	83.4	83	90.6	127	493	1500	68.1	39.3	125	81	28.4	46.5	207	206	759	1590	173	305	966	594
105, 132, 153	461	460	119	123	1110	2820	275	130	360	250	947	863	1620	1020	14500	13500	2650	3310	12500	7450
107	17.7	28	12.3	23.2	28.1	96.7	13.2	20.2	16	23	1	0	4.33	12.9	1	0	62.3	152	281	247
118	208	266	9.7	8.99	896	3490	66.2	62.9	227	407	113	114	243	231	4150	5650	1030	1460	4350	3460
119	10.8	14	37.3	93.2	324	1370	1	0	21	35.2	9.06	26.7	1	0	1	0	53.1	127	56.6	157
126, 129, 178	40.2	62	18.5	41.3	1	0	12.7	14.8	11	12.9	32.9	62.9	1.47	0.516	785	1570	105	210	912	666
128, 167,185	94.4	121	109	160	1650	5280	27.7	41.9	12	16	82.7	130	142	206	3780	7150	507	487	3300	1990
133, 134	70.8	142	19.9	26.7	1350	3650	6.78	17.3	1	0.378	83.1	289	50.7	129	694	1460	50.8	121	564	191
135, 144	30.5	45	3.4	4.95	129	537	4.56	10.7	113	176	95.9	139	3.93	7.74	1	0	71.6	208	84.8	178
136	2.87	4	6	11	209	614	7.67	20	20	36.6	60.9	164	89.7	192	1	0	8.05	25.4	26.6	72.5
137,176	279	256	30.7	30.1	38.9	90	118	74	119	76.9	20.9	58.9	105	308	548	2110	109	267	916	679
138,158	357	475	42.2	52.6	108	237	279	148	224	182	789	1170	685	672	7590	7730	1480	1770	7590	5020
141, 179	32.6	64	9.2	12.2	5.22	13.9	6.11	8.98	37	76.5	27.7	108	9.13	20.2	1.47	0.516	87.2	251	232	251
156, 171, 202,157,201	53.4	105	169	288	220	716	2	0	40	99.4	273	381	190	195	6440	16200	541	629	1790	1500
159, 187	139	165	1.9	1.91	116	399	245	139	202	174	252	327	296	291	13600	15100	1720	1490	6170	4250
170	35.3	63	8.6	17.6	400	1440	1	0	1	0	118	177	269	317	837	1610	230	399	1320	873
174	36.5	52	23.1	45.9	1	0	3.56	7.67	5	9.83	112	148	58.1	140	1	0	184	324	829	744
177	24.9	40	131	292	1	0	1	0	1	0	183	220	72.4	94.8	672	1400	46.8	129	675	484
180	100	107	61.2	134	314	1070	56.1	47.5	31	23.8	474	519	575	682	11900	10600	1610	1700	6960	4270
183	17.8	32	28.8	53.5	68.3	155	7.67	13.2	17	38.5	151	347	157	136	2020	3960	456	389	1530	948
194	6.64	15	1.44	1.33	1	0	1	0	1	0	85.4	120	234	293	3070	6800	397	573	2670	2080
195, 208	70.7	153	31.7	60	1580	4310	19.6	42.3	15	34.8	36.9	57.7	9.87	14	2860	6200	110	251	1440	1690
200	2.36	3	4.6	8.93	9.61	36.5	1	0	1	0	141	290	41.9	132	1	0	67.9	108	1	0
199	89.7	95	17.7	26.9	33.3	137	19.1	28.5	13	22.6	159	260	63.5	58.6	11800	30500	935	1360	3940	4100
205	2.84	4	49.2	69.2	333	905	1	0	1	0	18.3	34.4	12.3	40.8	1330	5140	50.8	99.1	83.9	132
206	107	215	58.1	146	68.3	246	1	0	15	36.7	67.8	111	185	211	7820	20700	552	956	4420	9520
207	1.73	1	4.4	7.66	16.4	65.3	1	0	1	0	1.94	4.01	10.2	18.6	230	888	12.9	43	189	383
209	206	365	9.3	14.5	152	463	20.4	58.3	34	86.6	65.1	116	184	172	1200	2400	103	151	1420	1890
77	8.88	9	2	0	18.6	26.3	4.78	2.17	14	31.2	4.22	6.43	8.56	3.76	64.9	24.8	9.38	7.96	23.3	20.3
81	1.75	1	1.5	0.707	19.5	29.3	1.78	1.09	2	1.13	3.06	3.52	5.63	5.56	60.6	28.7	8.92	9.09	8.13	4.64
126	7.22	10	3	2.83	10.7	11.3	5.56	3.28	11	23.3	8.11	9.36	36.9	117	77.4	39.3	11.4	4.66	34.8	18.9
169	3.95	2	3</																	

Supplemental Data Table for Trowbridge (Terrestrial Food Web)

Type and Sample size (n)	Soil (n=21)		Plants (n=28)		Terr. Inverts. (n=30)		Fresh Earthworms (n=18)		Depleted Earthworms (n=14)		Small Mammals (n=21)		Shrews (n=17)		House Wren Eggs (n=21)		House Wren Nestlings (n=18)		House Wren Adults (n=9)	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Lipid or TOC (%)	5.37	1.79	0.698	0.381	5.61	3.17	2.02	0.541	2.17	0.978	4.82	1.66	2.92	1.22	9.67	6.37	6.1	2.17	5.36	1.49
Total PCBs (mg/kg)	6.53	4.7	0.0232	0.0444	0.342	0.573	1.72	1.75	1.26	0.161	0.13	0.161	1.31	0.941	8.23	8.31	1.39	2.69	3.21	2.05
Total PCBs (pg/g)	653000	470000	23200	44400	342000	573000	172000	175000	126000	113000	130000	161000	1310000	941000	8230000	8310000	1390000	2690000	3210000	2050000
PCB Congener																				
4, 10	1250	3530	115	68.6	4820	11000	5050	3210	1810	530	505	474	4970	5140	1	0	4980		INT	
5, 8	13500	12600	203	285	54.7	214	362	358	757	1660	45.8	73.4	722	1790	1	0	1	0	295	278
6	4550	3780	96	233	1260	2100	400	565	693	1040	275	567	529	556	1	0	902	1760	1720	2450
9	1080	1760	523	1030	1990	3120	303	456	306	553	236	400	38.1	102	17200	58500	13800	16100	1020	655
15,17	78800	64500	256	563	3630	9810	7490	8690	5480	10600	1	0	1460	4070	1	0	2190	5680	17.2	48.7
16,32	93100	98800	311	540	932	1930	9150	9640	6760	13500	198	345	639	935	1	0	1	0	28.6	72.9
18	75600	73700	321	583	1420	2440	11900	13000	8180	15900	38.2	112	480	736	1	0	532	2250	41	106
19	11900	11700	69.5	88.1	1240	2540	770	484	876	1560	103	375	23.4	52.4	1	0	202	606	28.7	83
20,33,53	67000	51400	389	769	1420	3050	10300	9480	7660	13700	113	354	430	703	1	0	14.6	57.7	239	386
22	42500	41700	152	210	1220	2080	6080	6030	4650	5590	71.6	209	290	304	4360	12300	623	1490	1	0
25	17600	18000	501	2100	1100	1600	2310	2910	2090	2900	85.5	208	236	576	417	1500	175	408	936	970
26	43500	42700	231	398	1770	2970	7170	8200	5410	6800	53.6	142	2050	1800	2190	5390	809	721	85.6	160
27	10500	14900	44.1	66.1	519	2060	1650	1800	1340	2400	31.9	77.5	142	250	375	1420	1	0	329	983
28,31	32200	321000	1340	2780	17500	40600	74400	87400	59800	60700	1500	2050	15700	21600	323000	607000	31500	36100	39900	22700
37,41,42	575000	577000	1780	4010	11500	20200	140000	185000	86400	80100	378	561	7180	6530	43600	74700	36300	3400	5550	7770
40	64900	49600	216	411	1460	2360	12100	12000	8240	11100	404	495	758	227	671	306	395	125	245	
44	356000	285000	1050	2250	7340	14000	116000	138000	73500	73600	128	236	2820	3150	3940	8000	648	865	441	519
45	63200	54400	221	390	2390	3040	8360	9020	5930	10000	6.62	25.7	407	810	6810	18000	222	798	20	57
47,75	182000	154000	684	1350	13700	26500	52700	63400	37700	37400	1860	2850	45600	62800	242000	365000	35700	54400	50800	31200
49	345000	256000	1240	2560	9880	16100	123000	145000	90100	90000	280	275	3950	3750	87400	136000	11100	10200	14100	23500
52	454000	343000	1700	3140	14800	23600	167000	188000	126000	115000	529	579	9610	8580	35100	55000	3850	3520	3830	5410
56,92,84,90,101,113	556000	411000	1990	4100	28700	55600	179000	181000	112000	88300	1740	1450	15700	13800	366000	442000	58400	82400	67500	55200
66,95,96	634000	500000	2000	3950	30500	64900	174000	190000	122000	104000	3340	3900	60900	77800	982000	1330000	139000	230000	178000	56100
70	294000	243000	1050	2150	11500	19700	98500	119000	72200	78400	541	561	11900	16400	153000	302000	13300	11900	9860	12900
74	106000	97000	406	805	9330	20300	27900	37200	17100	18100	5060	15700	36400	51500	515000	710000	83900	171000	118000	49300
77, 85, 110, 120	400000	296000	1410	2800	16900	34500	111000	100000	96900	88100	740	674	14200	17700	729000	1350000	70100	109000	81200	99900
81,87,117	116000	91700	239	600	6750	15900	42400	30700	17900	22400	784	952	5590	4520	160000	157000	10700	13600	35700	24100
82, 151	76900	43400	247	531	2690	5410	19200	15300	12300	14000	104	227	972	740	18500	24100	2550	3340	1270	1220
83	28300	22500	136	148	1140	1750	5000	4670	3360	3810	9.29	38	330	380	640	1850	261	617	126	236
91	53000	32500	199	350	1590	2700	14100	13800	10200	10700	43.4	78.2	971	802	10600	14600	1690	1950	1240	1490
97	96200	71000	338	703	3490	6770	28700	23300	18100	16500	99	134	871	918	5410	7390	636	793	913	1130
99	151000	104000	696	1150	11700	21700	41500	39200	35100	31600	19500	37000	163000	124000	584000	522000	98800	208000	189000	137000
105, 132, 153	243000	157000	837	1870	24300	51800	52700	40300	42000	42000	25000	34200	234000	156000	1210000	909000	228000	470000	685000	560000
107	26200	18600	83.6	212	2480	5020	5030	3670	4710	5280	181	300	1960	2800	65300	51300	13400	30900	30200	21900
118	202000	153000	529	1270	20800	38600	38100	31300	36000	34900	10500	17600	132000	102000	1270000	1080000	226000	503000	590000	406000
119	12700	9410	33.3	82.5	1450	2790	2380	1730	1850	1770	68.9	127	2680	3500	20800	18200	3430	5740	4530	2670
126, 129, 178	18400	14300	59.8	159	1100	1580	2240	1070	3260	3360	857	1070	3420	3030	32700	23100	7580	17200	14200	10200
128, 167,185	48200	31800	317	683	8830	35700	6260	4080	5740	6630	2620	3310	31200	35200	127000	133000	20300	47700	67400	52900
133, 134	29000	22200	142	267	2960	11200	3680	4690	1620	1470	714	925	8320	9220	35800	37800	8180	18600	14500	12100
135, 144	40400	27900	117	214	1650	2610	6510	5870	4820	4580	22.7	45.1	536	481	19300	21600	3450	4480	2200	1780
136	17100	13000	69.6	103	352	897	2410	1190	1930	1540	7	27.5	280	725	1	0	62.6	200	73.7	140
137,176	39100	24800	114	292	5990	23700	5180	2030	6190	6650	1310	1820	12600	13500	62500	45800	10800	23500	25700	18900
138,158	196000	155000	512	1110	19200	44700	56600	55000	44900	38600	17900	23100	214000	168000	670000	478000	127000	267000	411000	373000
141, 179	37000	20200	122	324	1940	4270	6820	4340	6170	6200	83.8	96.3	1030	686	36000	26700	6440	11900	8010	6240
156, 171, 202,157,201	37300	23800	121	248	1950	4290	4750	4060	3300	4200	4220	4290	29900	33600	86400	51700	20900	52000	58500	48200
159, 187	45700	32800	122	282	8750	17900	40300	20100	35500	25300	5410	8600	44800	65900	392000	289000	80900	182000	217000	167000
170	32200	20500	77	226	1320	1620	3060	1920	2910	4160	3860	4860	31000	24900	57900	34300	12000	27300	42100	31400
174	29700	18900	89.3	180	8420	37300	4350	2690	3850	3990	492	620	12100	31400	31100	35700	6660	10700	5790	4230
177	22100	13000	107	273	3360	12800	2460	1340	2740	3290	1960	1500	16000	30900	35800	30200	7540	14700	15500	11600
180	51500	36000	133	298	3890	6630	4810	3210	6670	8680	7570	9480	84800	61600	205000	127000	46100	109000	167000	174000
183	21000	17100	62.5	164	2980	9220	1680	1460	2370	2080	1380	1750	16300	19100	46600	32300	8730	17900	23700	18900
194	13800	11600	21	61.6	1380	3000	1090	620	1290	1900	2200	2380	14900	14000	38600	22100	8830	19700	33600	31000
195, 208	10600	10400	47.5	154	1440	3190	845	823	569	820	835	899	3020	2730	11500	7870	2100	4520	5010	3080
200	1970	1580	27.2	102	113	385	238	297	792	2010	366	375	33.9	69.4	2360	3430	324	978	270	295
199	18200	12200	60.6	107	1060	1930	3210	1430	2940	2860	2230	2920	6600	12200	50900	32500	10900	24100	36700	32400
205	1140	1420	30.9	78.1	1500	7090	55.8	83.4	39.8	87.9	209	276	979	927	2080	3590	720	1660	10	